

THE INSOLUBLE CARBONACEOUS MATERIAL OF CM CHONDRITES AS POSSIBLE SOURCE OF DISCRETE ORGANICS DURING THE ASTEROIDAL AQUEOUS PHASE. H. Yabuta¹, L. Williams¹, G. Cody², and S. Pizzarello¹. ¹ Arizona State University, Chemistry & Biochemistry Dept., Tempe, AZ 85287-1604. ² Carnegie Institution of Washington, Geophysical Lab., Washington, DC 20015. pizzar@asu.edu.

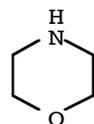
The larger portion of the organic carbon in carbonaceous chondrites (CC) is present as a complex and heterogeneous macromolecular material that is insoluble in acids and most solvents (IOM). So far, it has been analyzed only as a whole by microscopy (TEM) and spectroscopy (IR, NMR, EPR), which have offered an overview of its chemical nature, bonding, and functional group composition (*e. g.*, [1] and Fig 2). Chemical or pyrolytic decomposition has also been used in combination with GC-MS to identify individual compounds released by these processes [2 and ref.s therein]. Their value in the recognition of the original IOM structure resides in the ability to properly interpret the decomposition pathways for any given process.

We report here a preliminary study of IOM from the Murray meteorite that combines both the analytical approaches described above, under conditions that would realistically model the IOM hydrothermal exposure in the meteorite parent body. The aim is to document the possible release of water and solvent soluble organics, determine possible changes in NMR spectral features, and ascertain, by extension, the effect of this loss on the frame of the IOM residue.

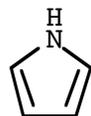
Fifteen grams of Murray powders, which had been water and solvent extracted, were demineralized by HF/HCl [3] treatment followed by HF/CsF washes [1]. Annealed gold capsules (~ 5x0.5 cm) were filled with aliquots (15-20mg) of the IOM and degassed water in equal proportion by weight, sealed, and inserted in a titanium pressure vessel that was brought to 300°C and 1Kbar in ~2hs, and kept to these T and P for six days. The hydrothermal conditions were chosen to mimic those that would allow diagenetic reactions, within the constraints of laboratory time.

The capsules were quenched and the wet powders collected with several rinses of water. The suspension was centrifuged and the supernatant separated, dried, derivatized with isopropanol 3NHCl and TFAA, and analyzed by GC-MS on a cyclodex column (Chrompack, 25m x 0.25mm). The powder was dried, extracted with 2 ml DCM/methanol and the extract also analyzed by GC-MS employing a DB17 column (J&W Scientific, 60m x 0.25mm) [4]. Water and solvents were 3x and 2x distilled, respectively.

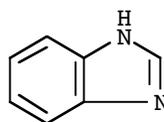
The main compounds identified in the water extracts are shown in the following diagram and Fig. 1. All, except morpholine, are present in several homologous species (*e. g.*, methyl, dimethyl/ethyl, and methylethyl benzimidazoles; C3-C16 dicarb acids).



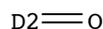
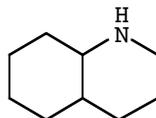
morpholine



pyrrole(s)



benzimidazole(s)



quinolinone(s)

The DCM/MeOH extracts were found to contain several molecular species. Some are common with other pyrolytic experiments [2], some are newly observed (Table 1).

Comparison between NMR spectra of the IOM prior and following the hydrothermal treatment of the powders is seen in Fig. 2. It shows the loss of a significant portion of the treated material aliphatic component.

The water-soluble compounds released during the IOM hydrothermal treatment are seen for the first time as products of decomposition of this material. They seem to fall under two general categories: small N-, and O-containing aromatic and cyclic molecules and linear dicarboxylic acids. The finding of the first group of compounds seem to suggest a possible genetic relationship between some of the molecules commonly found in liquid extracts and a more labile

portion of the IOM. The release is significant from a prebiotic perspective, given that the IOM represents, by far, the larger portion of exogenously delivered organic material.

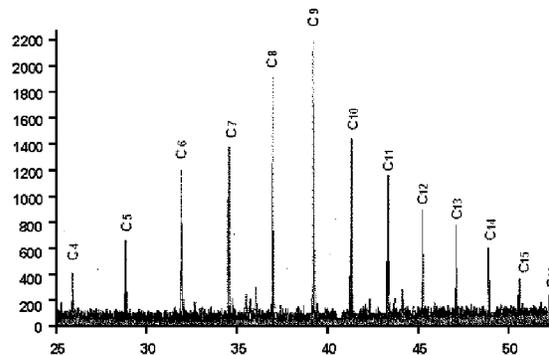


Fig.1. Single ion traces of linear dicarboxylic acids from the water extracts of hydrothermally treated-IOM, O-isopropyl esters.

The release of a large suite of dicarboxylic linear acids, which is accompanied by a few unsaturated species, is intriguing. The changes apparent in the NMR spectrum suggest a relation between these compounds and the aliphatic feature at about 70 ppm, which is reduced after the hydrothermal treatment. It is possible that this aliphatic component may contain long unsaturated hydrocarbon chains, either independent from the rest of the other material (e. g., with hydrolysable end groups such as CN) or attached to it.

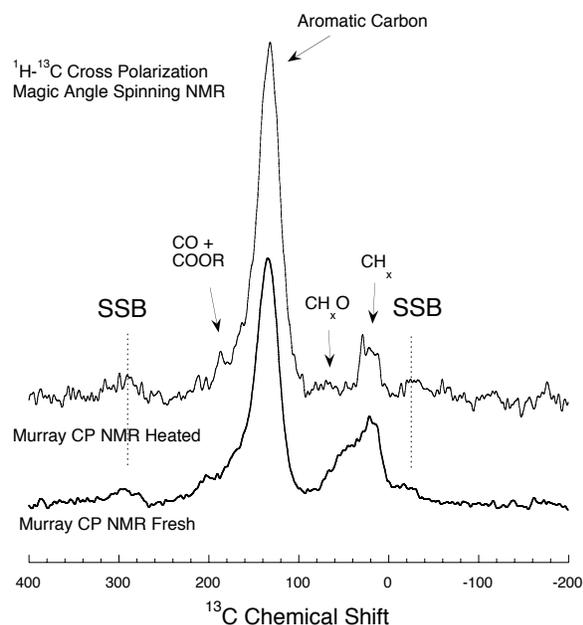


Fig. 2. ^1H - ^{13}C NMR spectra of treated and untreated Murray IOM

The aromatic compounds released by solvent extraction of the treated IOM have been found to be abundant and varied. The ones identified with reference standards and not seen in previous hydrous pyrolysis experiments are listed in the following table. It shows several alkylated homologues of both aromatic and N-, O-, and S-containing heteroaromatic compounds. The abundance of thiophenols is particularly interesting and confirms the predominance of sulfur chemistry in portions of the IOM [5]. The largest aromatics in these IOM extracts were benzopyrene and benzofluoranthene (FW 252).

Clearly, a portion of the IOM rather readily releases compounds that are commonly found in the soluble portion of the meteorite, as discussed at length by Sephton [2]. The findings also confirms the spectroscopic observations that CI and CM IOM comprises mainly small (smaller than C_{24} coronene) and highly substituted ring aggregates [6,7], with larger unprotonated structures making up, at most, only 10% of total aromatics [1].

Compound identified	Number of compounds
C_1 - C_4 naphthalenes	21
Biphenyl	
C_1 - C_2 biphenyls	6
Fluorene	
C_1 - C_2 fluorenes	12
Anthracene	
methylphenanthrenes	6
Benz[a]anthracene	
C_2 - C_3 phenols	14
Thiophenol	
C_1 - C_2 thiophenol	6
C_1 carbazoles	4

Although the formative relationship of these compounds in the soluble and insoluble organic portions of the meteorite remains uncertain, it is reasonable to assume that at least some of the soluble organics in the meteorite may have been released from the IOM during the parent body aqueous phase.

The hydrothermolytic method employed in this study for the Murray IOM models realistic parent body conditions and appears useful to explore the possibility of such genetic relationship, if any exists. Several additional experiments need to be conducted to test optimization of conditions, reproducibility of results, and the effect of inorganic phases on the hydrolytic process. They are in progress.

REFERENCES

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